



THE UNIVERSITY *of* EDINBURGH

## Edinburgh Research Explorer

# Using Mass Reconstruction along a Four-Site Transect as a Method to Interpret PM<sub>10</sub> in West-Central Scotland, United Kingdom

### Citation for published version:

Gibson, MD, Heal, MR, Bache, DH, Hursthouse, AS, Beverland, IJ, Craig, SE, Clark, CF, Jackson, MH, Guernsey, JR & Jones, C 2009, 'Using Mass Reconstruction along a Four-Site Transect as a Method to Interpret PM<sub>10</sub> in West-Central Scotland, United Kingdom', *Journal of the Air & Waste Management Association*, vol. 59, no. 12, pp. 1429-1436. <https://doi.org/10.3155/1047-3289.59.12.1429>

### Digital Object Identifier (DOI):

[10.3155/1047-3289.59.12.1429](https://doi.org/10.3155/1047-3289.59.12.1429)

### Link:

[Link to publication record in Edinburgh Research Explorer](#)

### Document Version:

Peer reviewed version

### Published In:

Journal of the Air & Waste Management Association

### Publisher Rights Statement:

Author's Post-print: subject to Restrictions below, author can archive post-print (ie final draft post-refereeing)

Restrictions:

12 month embargo for STM, Behavioural Science and Public Health Journals

18 month embargo for SSH journals

Publisher's Version/PDF: author cannot archive publisher's version/PDF

### General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [openaccess@ed.ac.uk](mailto:openaccess@ed.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



Post-print of peer-reviewed article published by Taylor & Francis.

Published article available at: <http://dx.doi.org/10.3155/1047-3289.59.12.1429>

Cite as:

Gibson, M.D., Heal, M.R., Bache, D.H., Hursthouse, A.S., Beverland, I.J., Craig, S.E., Clark, C.F., Jackson, M.H., Guernsey, J.R. and Jones, C. (2009) Using mass reconstruction along a four-site transect as a method to interpret PM<sub>10</sub> in West-Central Scotland, United Kingdom, *Journal of the Air & Waste Management Association* 59, 1429-1436.

## Using mass reconstruction along a four-site transect as a method to interpret PM<sub>10</sub> in west-central Scotland, UK

**Mark D. Gibson**

Department of Civil Engineering, University of Strathclyde, Glasgow, Scotland, UK

**Mathew R. Heal**

School of Chemistry, University of Edinburgh, Edinburgh, Scotland, UK.

**David H. Bache**

Department of Civil Engineering, University of Strathclyde, Glasgow, Scotland, UK

**Andrew S. Hursthouse**

School of Engineering and Science, University of the West of Scotland, Paisley, Scotland, UK.

**Iain J. Beverland**

Department of Civil Engineering, University of Strathclyde, Glasgow, Scotland, UK

**Susanne E. Craig**

Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada.

**Colin F. Clark**

The Highland Council, TEC Services, Glenurquhart Road, Inverness, Scotland, UK.

**Mike H. Jackson**

Department of Civil Engineering, University of Strathclyde, Glasgow, Scotland, UK

**Judith R. Guernsey**

Department of Community Health and Epidemiology, Dalhousie University, Halifax, Nova Scotia, Canada

**C. Jones**

Department of Mathematics and Statistics, Dalhousie University, Halifax, Nova Scotia, Canada

## ABSTRACT

Concurrent 24 hr samples of PM<sub>10</sub> were collected over a 10 day period in August 2000 at four sites along a transect in west-central Scotland, UK (passing from the coast through the city of Glasgow) in line with the prevailing south-westerly wind. Each sample was analyzed for, chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), calcium (Ca<sup>2+</sup>), iron (Fe) and organic hydrocarbon material (OHM). The contribution from elemental carbon (EC) was estimated. Sampling days were categorized according to local wind direction, synoptic flow and air mass back trajectories. Chemical mass balance reconstruction of the following PM<sub>10</sub> components was derived for each wind direction group and at each transect location: ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), sodium chloride (NaCl), gypsum (CaSO<sub>4</sub>), OHM, EC, soil/surface dusts and particle bound water. The results showed that PM<sub>10</sub> at the coastal site was dominated by the marine background (NaCl) compared with the urban sites which were dominated by local primary (elemental carbon and soil/resuspension) and secondary sources (NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and OHM). There was evidence of chloride depletion as NaCl aerosol passes over urban areas. There was also evidence of long-range transport of primary PM<sub>10</sub> (EC and OHM), for example at the coastal site from transport from Ireland. The work demonstrates how the general approach of combining mass reconstruction along a transect with other information such as wind/air-mass direction generates insight into the sources contributing to PM<sub>10</sub> over a spatial scale more extended than at a single receptor.

## IMPLICATIONS

This study highlights the utility of a multi-site transect aligned with the prevailing wind to identify changes in PM<sub>10</sub> chemical composition in air masses moving inland from a coastal region, through urban and peri-urban regions. Local, marine and long-range PM<sub>10</sub> components were identified. The chemical mass balance (CMB) calculation offers a pragmatic method for accounting for the major chemical sources contributing to PM<sub>10</sub> at a receptor. Interpreting the CMB of PM<sub>10</sub> is of policy relevance not only in helping identify sources but also because of the implications for health impacts.

## INTRODUCTION

Numerous studies published over the last 20 years have demonstrated a significant, linear association between the concentration of airborne particulate matter (PM) of median aerodynamic diameter less than 10 µm (PM<sub>10</sub>) and cardiopulmonary mortality and morbidity.<sup>1-3</sup> There appears to be no lower threshold in the dose-response between PM<sub>10</sub> concentrations and health effects.<sup>4</sup> Evidence suggests that particle size, number and chemical composition all ultimately determine the PM toxicological impact.<sup>5</sup>

PM<sub>10</sub> has many sources including anthropogenic, biogenic, geogenic, primary and secondary, local and long-range.<sup>6,7</sup> In order to determine the source contribution to PM<sub>10</sub> present at any given receptor it is necessary to gain as much knowledge as possible regarding the chemical composition, meteorological factors and an appreciation of the local and long-range sources impacting the receptor.<sup>8,9</sup> A number of methods to apportion PM<sub>10</sub> sources have been applied. These include deterministic approaches utilizing emission inventories and forward process modeling of the subsequent expected atmospheric concentration.<sup>10</sup> However these models are computationally and input-data demanding and often exclude contributions from

resuspended mineral dusts and marine-derived salt particles.<sup>9</sup> Other approaches use receptor models based upon multivariate statistics, including principal component analysis and the more sophisticated positive matrix factorization method.<sup>11-15</sup>

The chemical mass balance (CMB) approach to receptor modeling offers a relatively simple method for source apportionment of airborne PM. Knowledge of the CMB of PM not only helps to elucidate their source but can provide insight into their potential toxicology effects.<sup>16</sup> Additionally, the CMB information can aid air quality managers in the identification of particular anthropogenic emissions and subsequent management strategies to reduce them. A number of studies have used CMB to account for the collected PM<sub>10</sub> mass through measured and inferred major chemical constituents.<sup>17-19</sup> For example, a “pragmatic” mass closure model was applied to the source apportionment of PM<sub>1.0</sub>, PM<sub>2.5</sub>, and PM<sub>10</sub> collected at roadside, urban background and rural sites within and outside of Birmingham, UK.<sup>20</sup> This study concluded that the pragmatic CMB approach developed previously<sup>9</sup> was suitable for applying to new data sets at new locations and times.

## **AIM AND OBJECTIVES**

The aim of this study was to investigate chemical mass reconstruction as a method to gain insight into the factors (local emissions, long range transport, chemistry, etc.) influencing changes to PM<sub>10</sub> chemical composition along a transect through a major conurbation in the UK, specifically a SW to NE transect through the towns of Prestwick, Paisley, Glasgow and Cumbernauld in west-central Scotland. This is the first analysis of PM<sub>10</sub> for a transect in Scotland; with only one such analysis previously reported for the UK in SW England.<sup>21</sup>

The determination of ammonium, nitrate, sodium, calcium, chloride, sulfate and iron extracted from collected PM<sub>10</sub> is relatively straightforward, with recognized standard methods well documented in the literature.<sup>22-24</sup> However, the measurement of organic carbon (OC) and elemental carbon (EC) is problematic and there is no internationally-agreed standard analytical procedure.<sup>25</sup> Some current methods use a combination of thermal and optical techniques to differentiate between the OC and EC fractions within a sample of PM,<sup>26, 27</sup> but there are recognized problems with these methods.<sup>25, 28</sup> An alternative approach to estimate EC is via filter reflectance, but this is not a well quantified metric and suffers from issues of colored metal oxides and overloaded filters.<sup>29</sup> In this work, a loss on ignition approach was used to quantify total organic hydrocarbon material without requirement for further scale-up of an OC mass to total organic material mass.

## **METHODS**

### **Sampling**

Site selection was based on a transect aligned with the prevailing south-westerly wind direction;<sup>30</sup> with sites of contrasting coastal and urban environments including sub-urban zones upwind and downwind of a major urban centre. The sampling locations are shown in Figure 1 and descriptive data in Table 1. Prestwick is a small coastal town with low vehicle density. The sampler was located ~240 m from the shore. Although Prestwick International Airport is 1.5 km to the NNE, this is predominantly downwind of the site, and the airport has low passenger numbers compared with Glasgow International Airport (PIA: 905,000 in 2000; GIA: 6,924,000).<sup>31</sup> Apart from the airport and local traffic there are few local anthropogenic sources of PM<sub>10</sub> in Prestwick. Paisley is a larger urban area; the PM<sub>10</sub> sampler was centrally located on the Town Hall veranda, 4 m above the ground, and surrounded by urban roads

carrying a total of 10,000 vehicles d<sup>-1</sup>. The city of Glasgow is one of the largest urban conglomerations in the UK. The monitoring site was located in the centre of the city, but 30 m above street level in order to represent urban background. Glasgow has one of the highest vehicle densities in the UK due to the convergence of four major transport routes (M8, M80, M77 and M74). The M8 (which has the highest vehicle density) bisects Glasgow, the nearest point of which lies 860 m to the North West of the sampling site. There are two major railway termini in Glasgow which operate many diesel trains and are a considerable local source of elemental carbon. The predominantly downwind, sub-urban Cumbernauld monitoring site was located in a residential housing estate, adjacent to a road with a vehicle density of approximately 3,000 vehicles day<sup>-1</sup>.

Samples of PM<sub>10</sub> were collected concurrently at the four sites using US EPA Federal Reference Method filter samplers (Thermo Partisol 2000) each fitted with a US EPA approved SA246b Graseby Andersen PM<sub>10</sub> size-selective inlet and sampling at a flow rate of 16.7 l min<sup>-1</sup>. Samples were collected daily (starting at 8 am each day) from 7<sup>th</sup> - 17<sup>th</sup> August 2000.

### **Gravimetric and chemical analysis**

Samples were collected onto 47 mm diameter Whatman QMA quartz fibre filter with 0.6 µm diameter pore size. All filters were baked for 4 hours at 900°C in a muffle furnace before use, <sup>27</sup> then washed with 18 MΩ water, air dried in Petri dishes and placed in a dessicator to equilibrate for 48 h at 35-45% RH and 20 ± 2 °C prior to weighing. The filters, including blanks and six control filters, were weighed using a Sartorius MC5 microbalance following the protocol used by Heal et al. (2000). <sup>32</sup> An antistatic dissipater was employed to eliminate

weighing artifacts due to electrostatic charge. Gravimetric imprecision was calculated to correspond to  $1 \mu\text{g m}^{-3}$  for a 24 hr sample.

After re-weighing, the loaded filters were cut into thirds for chemical analysis: one third for the analysis of cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ ) and anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ), one third for the analysis of Fe (and other trace metals), and one third for indirect quantification of organic hydrocarbon material via mass loss on ignition at  $550^\circ\text{C}$ . Blank filters were used to check for background contamination for all analyses.

The filter portions for anion and cation determination were extracted with sonication into 5 ml of  $18 \text{ M}\Omega$  water and the solution analysed using a Dionex 2000i ion chromatography system with conductivity detection.<sup>8</sup> For cation analysis, a Hamilton PRP-X200 separation column (Phenomenex) was used, with a mobile phase of 4 mM nitric acid in 3:7 methanol:water at  $2 \text{ ml min}^{-1}$  flow rate. For anion analysis, a Dionex AS4A separation column preceded by a Dionex AG4A guard column was used, with a mobile phase of 1.8 mM  $\text{Na}_2\text{CO}_3$  and 1.7 mM  $\text{NaHCO}_3$  at  $2.5 \text{ ml min}^{-1}$  flow rate. A Dionex AMMS-II Anion Micro Membrane Suppressor was also employed, with a suppressor regenerant consisting of 25 mM  $\text{H}_2\text{SO}_4$  at a flow rate of  $6 \text{ ml min}^{-1}$ . In both cases, sample injection volume was 100  $\mu\text{l}$ . Iron and other trace metals were extracted from the filter using a mixed acid solution (5 ml) prepared by mixing concentrated nitric acid (65 ml), concentrated hydrochloric acid (185 ml) and diluting to 1 l with  $18 \text{ M}\Omega$  water. Four drops of concentrated perchloric acid were added to each 5 ml extract solution to aid the extraction process. The extracts were heated to  $40^\circ\text{C}$  for 2 hr, followed by 1 hr at  $90^\circ\text{C}$  and 2 hr at  $140^\circ\text{C}$ , then diluted to 10 ml with  $18 \text{ M}\Omega$  water and centrifuged at 10,000 rpm for 10 min. Metal concentrations were determined using ICP-OES (Jobin-Yvon 138) against 7-point standard calibration curves. The loss on ignition at  $550^\circ\text{C}$



provides a good estimate of the organic hydrocarbon content of PM, <sup>25, 27</sup> once corrected for loss of other volatile material (see later). It is recognized that some hydrocarbons may char rather than be driven off at this temperature and thus lead to an underestimation of OHM and an overestimation of EC (as derived here from the remaining “unaccounted for” mass of PM<sub>10</sub>).

### **Meteorological Data**

Temperature and relative humidity were recorded by each Partisol unit at each monitoring location. Other meteorological data (local wind direction, wind speed, and rainfall) were obtained from a Meteorological Station, 12.2 km west of the Glasgow monitoring site, 5.9 m above mean sea level. Synoptic charts were obtained from the Royal Meteorological Society ([www.rmets.org](http://www.rmets.org)) and used to classify wind direction according to “Lamb Weather Type” which contains eight main directional types: north, north-east, east, south-east, south, south-west, west and north-west <sup>30</sup>.

In addition, 5-day air mass back trajectories were calculated for arrival every 6 hours at the 950 hPa pressure level at each site using software and data at the British Atmospheric Data Centre ([badc.nerc.ac.uk](http://badc.nerc.ac.uk)). Air mass back trajectories are a useful tool for determining potential upwind sources of air pollutants reaching a receptor. <sup>33, 34</sup> Trajectories were visualized using the AGIS Geographical Information System <sup>35</sup> and categorized according to the broad geographical sector over which they had passed prior to reaching each site, with categorization defined by having at least 70% of the trajectory in that sector. <sup>30</sup>

## **RESULTS**

## **Meteorology**

Generally there was little rainfall during the study period. The 7, 8, 11, 12, 14 & 17 August 2000 had little rain, ranging between 2 – 4 mm; the remaining days were dry. The relative humidity was unusually high, between 95 and 100% at all of the monitoring locations, compared with the normal range 71 to 90% for this location.<sup>36</sup> The winds were predominately from the W and SW with fairly uniform wind speed around 3 m s<sup>-1</sup>.

## **Data groupings**

Daily air mass back trajectories could be consigned as described above to one of the following four categories, illustrated in Figure 2.

- WESTERLY– 5 days spent over the Atlantic before making landfall in the vicinity of Prestwick.
- SOUTH WESTERLY– from the Atlantic, then crossing Ireland from SW to NE before crossing the Irish Sea before making landfall in the vicinity of Prestwick.
- SOUTHERLY– from the Atlantic, through the Irish Sea avoiding Ireland, England and Wales before making landfall in the vicinity of Prestwick.
- EASTERLY– originating in Eastern Europe crossing the North Sea and central Scotland prior to reaching the transect sites.

Scrutiny of the local wind direction plots, Lamb weather types and chemical compositional data revealed similarities for certain sampling events, e.g. for the 7 and 8 August. These days were characterized by a westerly wind and low levels of PM<sub>10</sub> at Prestwick and Paisley. The air mass back trajectories confirmed similar geographical categorization. On this basis these

two days were grouped within the ‘Westerly’ classification. Days were grouped together only if both the meteorological parameters and the PM chemical composition were similar. This approach to grouping yielded the classification shown in Table 2. In the case of 14 August the local wind direction was highly variable and it was not possible to assign it into a well-defined category.

### **Transect PM<sub>10</sub> gravimetric concentrations**

The descriptive statistics of the PM<sub>10</sub> concentrations at each location along the transect are illustrated as box plots in Figure 3.

### **Mass Reconstruction**

The numerical procedures used to reconstruct PM<sub>10</sub> chemical composition from measured components are detailed in Table 3 and were based on the work of Harrison et al. (2003),<sup>9</sup> but with minor modifications. First, ammonium content was measured explicitly in this work so it was possible to calculate contributions from each of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub> and NaNO<sub>3</sub> independently. Secondly, total organic hydrocarbon material (OHM) was derived indirectly. The loss on ignition method drives off hydrocarbon species, but also drives off particle-bound water and volatilizes NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (which all have volatilization temperatures well below the 550°C temperature used). The mass of OHM in each sample is therefore the mass lost during the heating after subtraction of the masses of these latter components. Any other unidentified component that might also be lost on combustion will have small mass contribution compared to the major chemical species accounted for in Table 3. After accounting for all the other components detailed in Table 3, the remaining mass in each PM<sub>10</sub>

sample was assigned as EC. Thus, the CMB approach used here reconstructs the entire  $PM_{10}$  mass by definition. As discussed in the introduction, any organic hydrocarbon material that chars in situ on the filter rather than being driven off will erroneously be assigned as EC, but this is an issue also for more sophisticated thermo-optical OC-EC analysers.

The  $PM_{10}$  reconstructed mass (as defined above), for each site, and for each wind direction categorization, are shown in Figure 4, and expressed as percentage fractions of each reconstructed mass in Figure 5.

### **$PM_{10}$ Dispersion along the Transect**

SCREEN VIEW, a US EPA Gaussian Dispersion Screening model,<sup>37</sup> was used to assess the dispersion of primary surface emissions of  $PM_{10}$  from an upwind site downwind to the next site along the transect. The meteorology observed during SW airflow was used in the model as this is in alignment with the transect sites. The model assumes that  $PM_{10}$  does not change state over the timescale modelled and that wind direction remains constant. The model does not include background and/or long-range transported  $PM_{10}$  sources. Additionally, only simple terrain can be incorporated into the model whereas there are hills between Prestwick and Paisley. The terrain from Paisley to Glasgow to Cumbernauld does however fit the ‘simple’ category. Despite these simplifications, the model provides some useful insight into the extent to which dispersion of primary  $PM_{10}$  emissions at the upwind site can impact the downwind receptor. Figure 6 illustrates the modelled dispersion of primary emissions of  $PM_{10}$  in Glasgow downwind towards the Cumbernauld site. The modelled contributions, on average, to the total  $PM_{10}$  concentrations at each site due to primary  $PM_{10}$  emissions from the

adjacent upwind urban area were as follows: Prestwick to Paisley =  $0.34 \mu\text{g m}^{-3}$ , Paisley to Glasgow =  $3.6 \mu\text{g m}^{-3}$ , Glasgow to Cumbernauld =  $8.5 \mu\text{g m}^{-3}$ .

## DISCUSSION

Although the discussion here necessarily focuses on the data obtained in this study, it demonstrates the general approach that can be taken to analyzing PM compositional data from along a transect.

A multivariate analysis of variance confirmed the visual impressions gained from Figures 3-5; namely that sampling site has a significant effect upon the mean concentrations of NaCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ , OHM, soil and EC in sampled  $\text{PM}_{10}$  ( $p = 0.015$ ), and that wind direction also has a significant effect upon the mean concentrations of the same components ( $p = 0.014$ ). The interpretations of the detail of the observed differences in  $\text{PM}_{10}$  composition sampled along the transect are given below.

Figure 3 shows that the highest average  $\text{PM}_{10}$  observed was in Cumbernauld ( $\bar{X} \pm 1 \text{ SD} = 40.0 \pm 10 \mu\text{g m}^{-3}$ ) and Glasgow ( $30 \pm 15 \mu\text{g m}^{-3}$ ). As shown in Figure 4 and 5,  $\text{PM}_{10}$  at these two locations are dominated by EC, OHM, Soil/Dust,  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and associated particle-bound water. The lowest  $\text{PM}_{10}$  concentrations were observed at Prestwick under the conditions of the Westerly air flow prevailing on 7 and 8 August ( $7.6 \mu\text{g m}^{-3}$ ), the South Westerly air flow prevailing on 11, 15, 16 & 17 August ( $7.3 \mu\text{g m}^{-3}$ ) and the Southerly air flow prevailing on 12 August ( $8.8 \mu\text{g m}^{-3}$ ). Figures 4 and 5 show that under Westerly air flow the  $\text{PM}_{10}$  in the coastal town of Prestwick is dominated by NaCl, presumably of marine origin from the Atlantic. The “outlier”  $\text{PM}_{10}$  concentration for Paisley shown in Figure 3 is

terminology assigned by the plotting package and should not be interpreted as erroneous since the gravimetric value is consistent with the independent measurements of the major chemical components of this sample. This datum is for the 13 Aug, the one day of easterly air flow, when air masses arriving at Paisley had previously passed over Glasgow, Central Scotland and the European mainland.

The composition of  $PM_{10}$  at Prestwick and Paisley, for EC, OHM,  $NH_4NO_3$  and  $(NH_4)_2SO_4$ , was highly significant different ( $p < 0.0005$ ) under Easterly air flow compared to all the other wind direction groups (Figures 4 and 5). This suggests upwind sources of primary and secondary ‘aged’ aerosol originated from continental Europe and Central Scotland. Figure 4 and 5 also show evidence of transport of EC and OHM advected from Ireland during the period 11, 15, 16 and 17 August; these components have low concentrations at Prestwick for westerly air flow directly from the North Atlantic but missing Ireland (7 and 8 August), but show a highly significant increase ( $p < 0.0005$ ) during south-westerly air flow which has crossed Ireland and passed over the city of Belfast en route to Prestwick. Westerly air flow on 10 August appears also to have entrained some secondary aerosol (as revealed by  $NH_4NO_3$ ) before arrival at Prestwick. The air mass back trajectories showed that the air mass arriving on the 10 August passed close to the North of Ireland coastline as compared with the Westerly airflows on the 7 and 8 August. Despite this,  $PM_{10}$  on 10 August at Prestwick and Paisley still contained predominant proportion from NaCl, demonstrating the significant contribution that marine aerosol makes to the total  $PM_{10}$  observed in maritime regions. Figures 4 and 5 also show that EC, OHM,  $NH_4NO_3$  and  $(NH_4)_2SO_4$  concentrations at Prestwick and Paisley are somewhat elevated during Southerly air flow (e.g. 9 August) compared with Westerly and South-Westerly air flow, presumably due to advection of  $PM_{10}$  from England to all the sites under these conditions.

An interesting observation is that, for most of the sampling campaign, the NaCl content of the PM<sub>10</sub> declines substantially between Paisley and Glasgow. It is assumed this is due to the numerous reactions that are known to occur between NO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NaCl which lead to removal of Cl from the particle phase via formation of gaseous HCl and ClNO<sub>2</sub>,<sup>38, 39</sup> for example,  $\text{NaCl}_{(s)} + \text{HNO}_{3(g)} \rightarrow \text{NaNO}_{3(s)} + \text{HCl}_{(g)}$ . The loss of NaCl at Glasgow and Cumbernauld is supported by the greater NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentrations in Glasgow and Cumbernauld than Prestwick and Paisley (except for Easterly air flow where they are comparable due to advection from more polluted terrestrial areas).

Another interesting observation is the general trend for increased “soil/resuspended” component concentration from Prestwick → Paisley → Glasgow (Figure 4); this source contributes ~20% of the PM<sub>10</sub> composition in Glasgow and Cumbernauld. The increasing trend is evidence that the soil component originates principally from local sources during passage along the transect, most likely vehicle-induced re-suspension of surface soil on roads from the increased traffic density in the Glasgow and Cumbernauld area. There was no discernable site specific or wind directional trend associated with the gypsum component, since this is a marker of site-specific construction activity.

A further feature is the increase in the OHM/EC ratio moving inland from the coast. The OHM/EC ratios for all Prestwick and Paisley samples ranged from 0.20 to 0.88, whereas the OHM/EC ratios for Glasgow and Cumbernauld ranged from 0.89 to 1.00. The OHM/EC ratios observed for Glasgow and Cumbernauld are similar to those reported for other urban environments.<sup>25, 40</sup> Figure 5 shows that the OHM has some spatial uniformity in Prestwick, Glasgow and Cumbernauld, accounting for approximately 20%, on average, of total PM<sub>10</sub>.

This is also consistent with the findings of Jones and Harrison (2005) who observed that OC contributes ~22%, on average to total  $\text{PM}_{10}$  with reasonable spatial uniformity across other sites in the UK. <sup>41</sup> The OHM will comprise both locally primary emitted OHM and secondary OHM generated on the regional scale. The lightly traffic influenced coastal Prestwick site in this study shows lower OHM concentrations.

The simple Gaussian dispersion modelling showed that approximately  $8 - 9 \mu\text{g m}^{-3}$  of primary-emitted  $\text{PM}_{10}$  may be advected to Cumbernauld from Glasgow (for Westerly and South Westerly wind directions). Although Figure 6 shows that primary  $\text{PM}_{10}$  emissions disperse rapidly in the first 10 km downwind, Glasgow is within this 10 km zone from Paisley so does inherit a significant  $\text{PM}_{10}$  contribution from Paisley (~12% of the mean  $\text{PM}_{10}$  concentration in Glasgow). Similarly, Cumbernauld, although 17 km downwind of Glasgow, receives considerable primary  $\text{PM}_{10}$  import from Glasgow approximately 20% of the total on average, due to the high primary emissions within Glasgow. These observations obviously have implications for effectiveness of local air quality management strategies.

Although the data for this study were collected a number of years previously and emissions of primary PM, and of precursors contributing to secondary PM, have generally continued to decline in the UK and most of Europe, the major sources and atmospheric processes contributing to receptor-measured  $\text{PM}_{10}$  in the UK are broadly unchanged <sup>7</sup>. Thus whilst the primary purpose here is to demonstrate a methodological approach, it is anticipated that the specific results for the example study area remain valid also.



## CONCLUSIONS

This work demonstrates how simultaneous sampling of PM<sub>10</sub> along a transect, coupled with chemical mass balance, provides insights into the changes in PM<sub>10</sub> chemical composition with prevailing wind direction; in this study, for example, on moving inland from the west coast of Scotland through the major conurbation of Glasgow. The upwind coastal site at Prestwick revealed the marine and long-range transport components whilst PM<sub>10</sub> in the city of Glasgow, and at the downwind site near Cumbernauld included substantial primary material associated with high-density urban areas (EC, OHM, resuspended material). There was clear evidence of chloride loss from PM<sub>10</sub> moving inland. Under Easterly air flow, a component of long-range transport of secondary aged aerosol (NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) from continental Europe was apparent. Studies of the design reported can contribute to policy development by helping identify sources contributing to PM<sub>10</sub> over a spatial scale more extended than at a single receptor and thus to more informed targeting of abatement measures.

## ACKNOWLEDGEMENTS

We are grateful to the Department of Air Quality, Glasgow City Council, UK for supporting this research and to Dave Reeve, Reeve Scientific, for the loan of a PM<sub>10</sub> sampler. We are also grateful to the Department of Civil Engineering, University of Strathclyde for funding this research. Gavin King, Environment Canada Science Horizons Intern, Department of Community Health and Epidemiology, Dalhousie University is acknowledged for providing Figure 1. Finally, we would like to acknowledge Thermo and Perkin-Elmer for continued support of our research activity.

## REFERENCES

1. Dockery, D. W.; Stone, P. H., Cardiovascular Risks from Fine Particulate Air Pollution. *The New England Journal of Medicine*. **2007**, 356, 511-513.
2. Stieb, D. M.; Judek, S.; Burnett, R. T., Meta-Analysis of Time-Series Studies of Air Pollution and Mortality: Effects of Gases and Particles and the Influence of Cause of Death, Age, and Season. *Journal of the Air & Waste Management Association*. **2002**, 52, 470-484.
3. Donaldson, K.; Stone, V.; Seaton, A.; MacNee, W., Ambient Particle Inhalation and the Cardiovascular System: Potential Mechanisms. *Environmental Health Perspectives*. **2001**, 106, 523-527.
4. Stieb, D. M.; Burnett, R. T.; Smith-Doiron, M.; Brion, O.; Shin, H. H.; Economou, V., A New Multipollutant, No-Threshold Air Quality Health Index Based on Short-Term Associations Observed in Daily Time-Series Analyses. *Journal of the Air & Waste Management Association*. **2008**, 58, 435-450.
5. Mills, N. L.; Robinson, S. D.; Fokkens, P. H. B.; Leseman, D. L. A. C.; Miller, M. R.; Anderson, D.; Freney, E. J.; Heal, M. R.; Donovan, R. J.; Blomberg, A.; Sandström, T.; MacNee, W.; Boon, N. A.; Donaldson, K.; Newby, D. E.; Cassee, F. R., Exposure to Concentrated Ambient Particles does not affect Vascular Function in Patients with Coronary Heart Disease. *Environmental Health Perspectives*. **2008**, (doi:10.1289/ehp.11016).
6. Harrison, R. M.; Jones, A. M.; Lawrence, R. G., Major component composition of PM<sub>10</sub> and PM<sub>2.5</sub> from roadside and urban background sites. *Atmospheric Environment*. **2004**, 38, 4531-4538.
7. AQEG, Particulate Matter in the United Kingdom. *DEFRA London*. **2005**.
8. Ward, T. J.; Rinehart, L. R.; Lange, T., The 2003/2004 Libby, Montana PM<sub>2.5</sub> Source Apportionment Research Study. *Aerosol Science and Technology*. **2006**, 40, 166-177.
9. Harrison, R. M.; Jones, A. M.; Lawrence, R. G., A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. *Atmospheric Environment*. **2003**, 37, 4927-4933.
10. APEG, Source Apportionment of Airborne Particulate Matter in the UK, Air Pollution Expert Group. *Report to the Department of the Environment, Transport and the*

*Regions, the Welsh Office, the Scottish Office and the Department of the Environment (NI). 1999.*

11. Song, X.-H.; Polissar, A. V.; Hopke, P. K., Sources of fine particle composition in the northeastern US. *Atmospheric Environment*. **2001**, *35*, 5277-5286.
12. Ilacqua, V.; Hanninen, O.; Saarela, K.; Katsouyanni, K.; Kunzli, N.; Jantunen, M., Source apportionment of population representative samples of PM<sub>2.5</sub> in three European cities using structural equation modelling. *Science of The Total Environment*. **2007**, *384*, 77-92.
13. Eberly, S., EPA PMF 1.1 User's Guide. *U.S. Environmental Protection Agency National Exposure Research Laboratory Research Laboratory Triangle Park, NC 27711*. **2005**, <http://epa.gov/heasd/products/pmf/pmf.htm>.
14. Jeong, C.-H.; Evans, G. J.; Dann, T.; Graham, M.; Herod, D.; Dabek-Zlotorzynska, E.; Mathieu, D.; Ding, L.; Wang, D., Influence of biomass burning on wintertime fine particulate matter: Source contribution at a valley site in rural British Columbia. *Atmospheric Environment*. **2008**, *42*, 3684-3699.
15. Paatero, P.; Hopke, P. K., Discarding or downweighting high-noise variables in factor analytic models. 8<sup>th</sup> International Conference on Chemometrics and Analytical Chemistry. *Analytica Chimica Acta*. **2003**, *490*, 277-289.
16. Laden, F.; Neas, L. M.; Dockery, D. W.; Schwartz, J., Associations of fine particulate matter from different sources with daily mortality in six US cities. *Environmental Health Perspectives*. **2000**, *108*, 941-948.
17. Watson, J. G.; Chow, J. C.; Lu, Z.; Fujita, E. M.; Lowenthal, D. H.; Lawson, D. R., Chemical mass balance source apportionment of PM<sub>10</sub> during the southern California air quality study. *Aerosol Science and Technology*. **1994**, *21*, 1-36.
18. Brook, J. R.; Dann, T. F.; Burnett, R. T., The Relationship Among TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and Inorganic Constituents of Atmospheric Particulate Matter at Multiple Canadian Locations. *Journal of the Air & Waste Management Association*. **1997**, *47*, 2-19.
19. Malm, W. C.; Hand, J. L., An examination of the physical and optical properties of aerosols collected in the IMPROVE program. *Atmospheric Environment*. **2007**, *41*, 3407-3427.
20. Yin, J.; Harrison, R. M., Pragmatic mass closure study for PM<sub>1.0</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> at roadside, urban background and rural sites. *Atmospheric Environment*. **2008**, *42*, 980-988.

21. Turnbull, A. B.; Harrison, R. M., Major component contributions to PM<sub>10</sub> composition in the UK atmosphere. *Atmospheric Environment*. **2000**, *34*, 3129-3137.
22. Chan, Y. C.; Simpson, R. W.; McTainsh, G. H.; Vowles, P. D.; Cohen, D. D.; Bailey, G. M., Source apportionment of PM<sub>2.5</sub> and PM<sub>10</sub> aerosols in Brisbane (Australia) by receptor modelling. *Atmospheric Environment*. **1999**, *33*, 3251-3268.
23. Ho, K. F.; Lee, S. C.; Chan, C. K.; Yu, J. C.; Chow, J. C.; Yao, X. H., Characterization of chemical species in PM<sub>2.5</sub> and PM<sub>10</sub> aerosols in Hong Kong. *Atmospheric Environment*, **2003**, *37*, 31-39.
24. Querol, X.; Alastuey, A.; Ruiz, C. R.; Artinano, B.; Hansson, H. C.; Harrison, R. M.; Buringh, E.; ten Brink, H. M.; Lutz, M.; Bruckmann, P.; Straehl, P.; Schneider, J., Speciation and origin of PM<sub>10</sub> and PM<sub>2.5</sub> in selected European cities. *Atmospheric Environment*. **2004**, *38*, 6547-6555.
25. Harrison, R. M.; Yin, J., Sources and processes affecting carbonaceous aerosol in central England. *Atmospheric Environment*. **2008**, *42*, 1413-1423.
26. NIOSH, ELEMENTAL CARBON (DIESEL PARTICULATE). *NIOSH Method 5040 Manual of Analytical Method (NMAM), Fourth Edition*. **1999**.
27. Chow, J. C.; Watson, J. G.; Lyle, C. P.; William, R. P.; Clifton, A.; Richard, G. P., The DRI Thermal/Optical reflectance carbon Analysis system: Description, Evaluation and Applications in U.S. Air Quality Studies. *Atmospheric Environment*. **1993**, *27A*, 1185-1201.
28. Chow, J. C.; Watson, J. G.; Chen, L.-W. A.; Arnott, W. P.; Moosmuller, H., Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols. *Environ. Sci. Technol.* **2004**, *38*, 4414-4422.
29. Cyrys, J.; Heinrich, J.; Hoek, G.; Meliefste, K.; Lewné, M.; Gehring, U.; Bellander, T.; Fischere, P.; van Vliet, P.; Brauer, M.; Wichmann, H.-E.; Brunekreef, B., Comparison between different traffic-related particle indicators: Elemental carbon (EC), PM<sub>2.5</sub> mass, and absorbance. *Journal of Exposure Analysis and Environmental Epidemiology*. **2003**, *13*, 134-143.
30. Buchanan, C. M.; Beverland, I. J.; Heal, M. R., The influence of weather-type and long-range transport on airborne particle concentrations in Edinburgh, UK. *Atmospheric Environment*. **2002**, *36*, 5343-5354.
31. Scottish Executive, Scottish Transport Statistics. *A Scottish Executive National Statistics Publication, No. 20*. **2001**,  
<http://www.scotland.gov.uk/stats/bulletins/103/103-00.asp>, Table 9.

32. Heal, M. R.; Beverland, I. J.; McCabe, M.; Hepburn, W.; Agius, R. M., Intercomparison of five PM<sub>10</sub> monitoring devices and the implications for exposure measurement in epidemiological research. *Journal of Environmental Monitoring*. **2000**, 2, 455-461.
33. Beverland, I. J.; Tunes, T.; Sozanska, M.; Elton, R.; Agius, R.; Heal, M., Effect of long-range transport on local PM<sub>10</sub> concentrations in the UK. *International Journal of Environmental Health Research*. **2000**, 10, 229-238.
34. Heal, M. R.; Hibbs, L. R.; Agius, R. M.; Beverland, I. J., Total and water-soluble trace metal content of urban background PM<sub>10</sub>, PM<sub>2.5</sub> and black smoke in Edinburgh, UK. *Atmospheric Environment*. **2005**, 39, 1417-1430.
35. AGIS, AGIS v1.58 Software. **2001**.
36. BADC, British Atmospheric Data Centre. *Space Science and Technology Department R25, Room 2, 119, Rutherford Appleton Laboratory*. **2002**, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, England, UK.
37. Lakes Environmental, SCREEN VIEW Screening Air Disperison Model. **2002**.
38. Zhuang, H.; Chan, C. K.; Fang, M.; Wexler, A. S., Formation of nitrate and non-sea-salt sulfate on coarse particles. *Atmospheric Environment*. **1999**, 33, 4223-4233.
39. Harrison, R. M.; Msibi, M. I.; Kitto, A. M. N.; Yamulki, S., Atmospheric chemical transformations of nitrogen compounds measured in the north sea experiment, September 1991. *Atmospheric Environment*. **1994**, 28, 1593-1599.
40. Castro, L. M.; Pio, C. A.; Harrison, R. M.; Smith, D. J. T., Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. *Atmospheric Environment*. **1999**, 33, 2771-2781.
41. Jones, A. M.; Harrison, R. M., Interpretation of particulate elemental and organic carbon concentrations at rural, urban and kerbside sites. *Atmospheric Environment*. **2005**, 39, 7114-7126.

## ABOUT THE AUTHORS

At the time this research was conducted, Mark Gibson was an assistant professor in Environmental Health in the Department of Civil Engineering at the University of Strathclyde, researching the source apportionment of atmospheric aerosols. Mark is now a senior research scientist with the Atlantic RURAL Centre, also holding a Teaching Faculty positioning in Community Health and Epidemiology at Dalhousie University. Mathew Heal is a senior lecturer in environmental chemistry, specializing in atmospheric and air quality measurements, at the School of Chemistry, University of Edinburgh. David Bache is an air pollution and water treatment specialist and reader in Public Health Engineering in the Department of Civil Engineering, University of Strathclyde. Andrew Hursthouse is Professor of Environmental Geochemistry researching contaminant behavior in relation to air pollution and contaminated soils and sediments and is based in the School of Engineering and Science, University of the West of Scotland. Iain Beverland is an environmental health and air pollution specialist, and senior lecturer in Environmental Health, Department of Civil Engineering, University of Strathclyde. Susanne Craig is a specialist in optical oceanography and a research associate in the Department of Oceanography, Dalhousie University. Colin Clark is the Head of Waste Management, The Highland Council, TEC Services, Inverness, Scotland, and formerly a senior lecturer at the University of Strathclyde. Mike Jackson is a professor emeritus and former Head of the Division of Environmental Health, Department of Civil Engineering, University of Strathclyde. Judy Guernsey is a specialist in environmental health, associate professor at the Department of Community Health and Epidemiology, Dalhousie University and director of the Atlantic RURAL Centre. Chris Jones specializes in the analysis of satellite imagery and works as a statistical consultant for both the Mathematics and Statistics department and the Oceanography department at Dalhousie University. Please address correspondence to Mark Gibson, Room 401, Community Health and Epidemiology, Dalhousie University, 5790 University Avenue, Halifax, Nova Scotia, Canada, B3H 1V7; phone: +1-902-494-7019; fax +1-902-494-1597; e-mail: mark.gibson@dal.ca.

## Tables

Table 1. Summary of PM<sub>10</sub> monitoring site characteristics

Location	Site Characteristics	Site co-ordinates Latitude Longitude	Distance from adjacent site running SW to NE (km)	Elevation (m)	Pop <sup>n</sup>	Area (km <sup>2</sup> )
Prestwick	Coastal	55.49527°N 4.61768°W	0	4.9	15,476	10
Paisley	Urban	55.84524°N 4.42147°W	42	9.0	77,000	40
Glasgow	Urban	55.86175°N 4.24453°W	8	30.0	611,440	110
Cumbernauld	Sub-urban	55.93493°N 4.03643°W	17	86.0	51,500	50

Table 2. Data group categories

Data group	Dates (August 2000)
Westerly air flow	10
Westerly air flow	7 & 8
South Westerly air flow	11, 15, 16, & 17
Southerly air flow	9
Southerly air flow	12 (spanning Saturday & Sunday)
Easterly air flow	13
14 August could not be categorized due too much deviation in the air flow	

Table 3. Adjustment factors used in mass closure (adapted from Harrison et al., 2003)

Analyte	Conversion to	Numerical factor
Sulfate	$(\text{NH}_4)_2\text{SO}_4$	Take measured mass of $\text{SO}_4$ and subtract ( $2.4 \times \text{Ca}$ ) to yield a corrected $\text{SO}_4$ not contained within Gypsum. Multiply result by 1.375
	Particle Bound Water	Multiply $(\text{NH}_4)_2\text{SO}_4$ by 0.29
Ammonia	$\text{NH}_4\text{NO}_3$	Take measured mass of $\text{NH}_4$ and subtract ( $0.375 \times$ corrected mass of $\text{SO}_4$ as above) to yield $\text{NH}_4$ not associated with $(\text{NH}_4)_2\text{SO}_4$ . Multiply result by 4.44 to yield $\text{NH}_4\text{NO}_3$
	Particle Bound Water	Multiply $\text{NH}_4\text{NO}_3$ by 0.29
Nitrate	$\text{NaNO}_3$	Take measured mass of $\text{NO}_3$ and subtract ( $0.775 \times$ derived mass of $\text{NH}_4\text{NO}_3$ ) to yield $\text{NO}_3$ not associated with $\text{NH}_4\text{NO}_3$ . Multiply result by 1.375 to yield $\text{NaNO}_3$
Chloride	$\text{NaCl}$	Multiply Cl by 1.648
Calcium	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum)	Multiply Ca by 4.30
Iron	Soil/road dust	Multiply Fe by 7.50
Mass lost on filter combustion	Organic Hydrocarbon Material	Take mass of material lost on combustion and subtract (mass of $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{NO}_3$ + associated particle bound water).
Unexplained mass	Elemental Carbon	Remaining mass ~ elemental carbon



Figure 1: Map of the PM10 sampling locations.



Figure 2: Four wind direction groups defined during sampling between August 7 and 17, 2000.

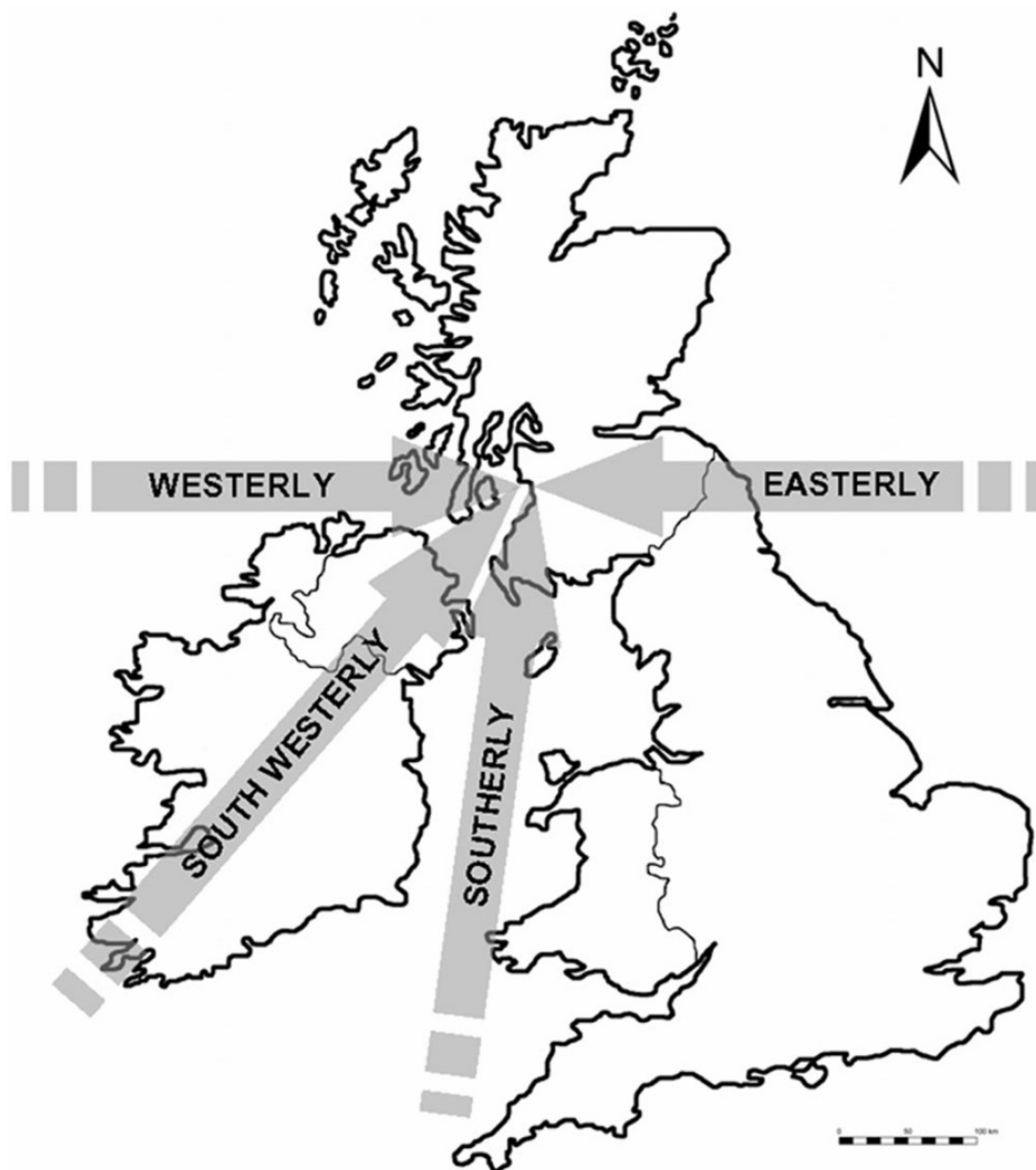


Figure 3: Box plots of the PM<sub>10</sub> concentrations measured at each site in the transect over the period August 7–17, 2000.

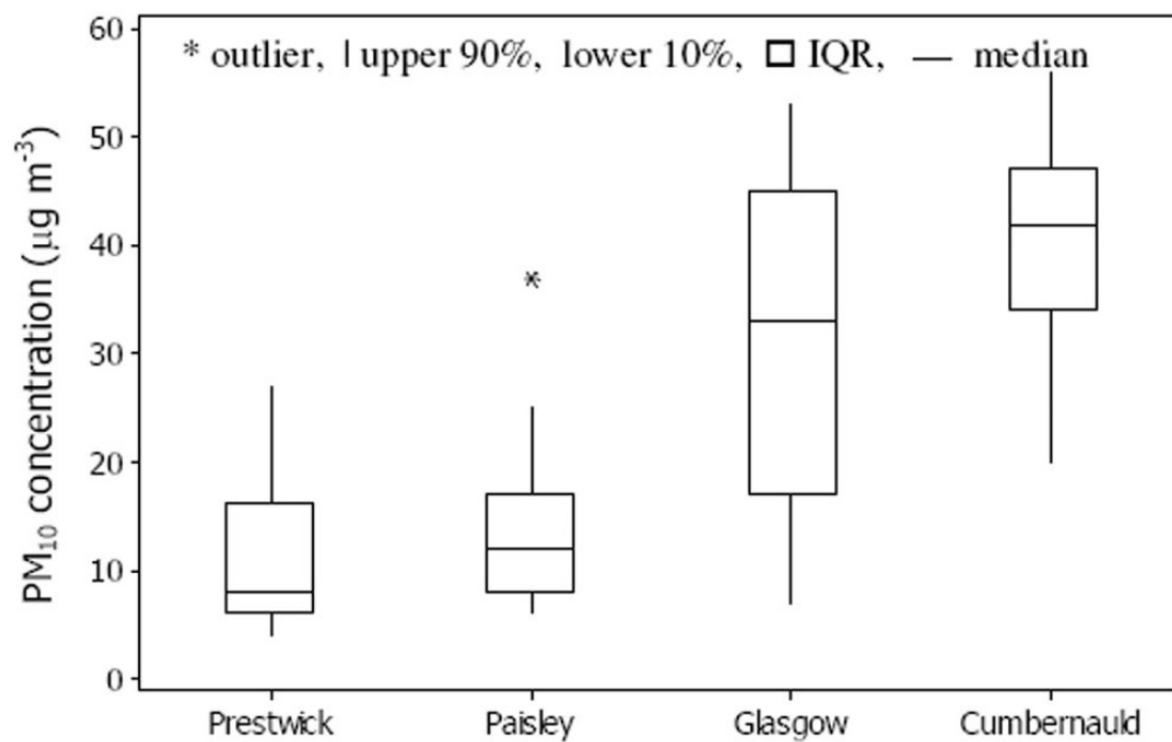


Figure 4: PM<sub>10</sub> reconstructed mass by site and by wind direction group (August 7–17, 2000).

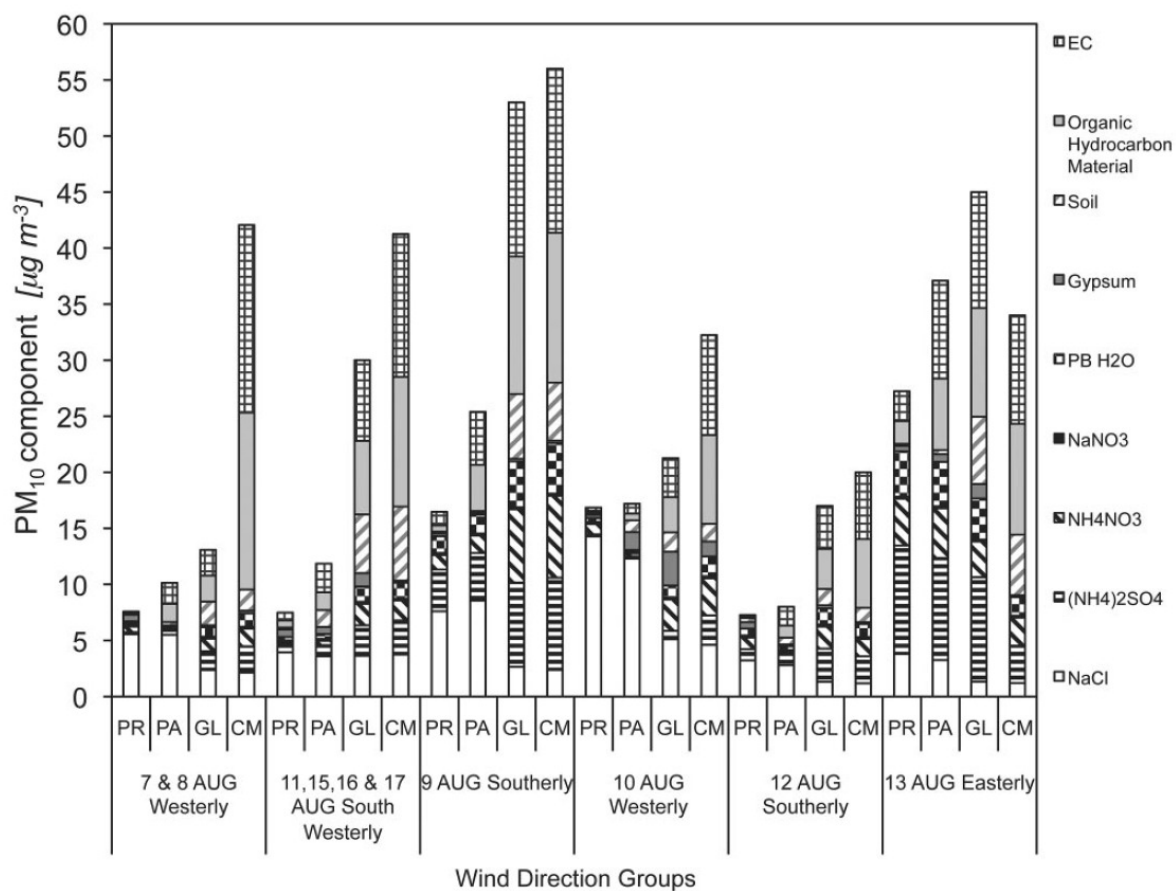


Figure 5: Percent reconstructed PM<sub>10</sub> mass by site and wind direction group (August 7–17, 2000).

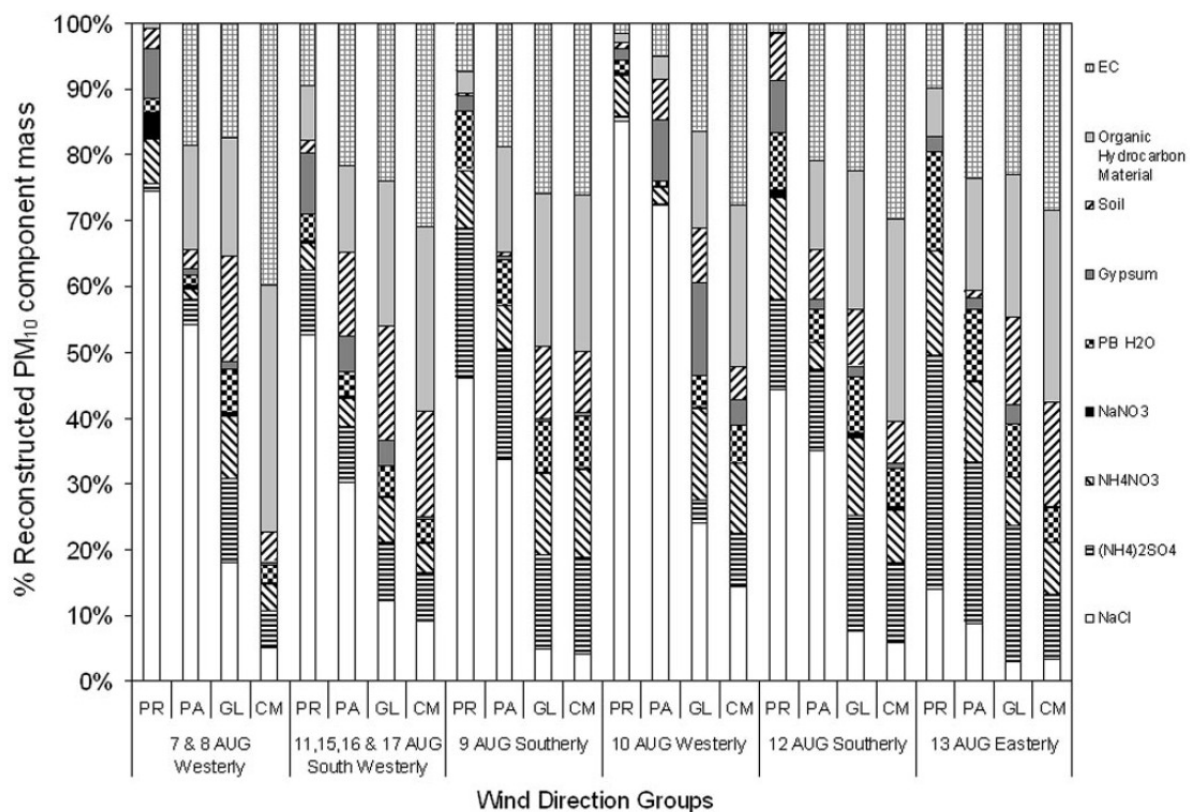


Figure 6: Screen view modeled  $PM_{10}$  dispersion downwind of Glasgow during southwesterly airflow. The initial rise in  $PM_{10}$  concentrations arises because Glasgow is a large area source and air continues to pick up  $PM_{10}$  primary emissions downwind from the center of the city before dispersion dominates beyond the conurbation boundary.

